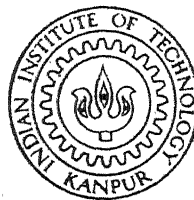


ALMORA MAGNESITE

By
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DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPU
NOVEMBER, 1976

ALMORA MAGNESITE

A Thesis Submitted
in partial fulfilment of the requirements
for the Degree of
MASTER OF TECHNOLOGY

6/11/76

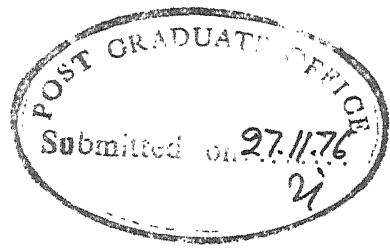
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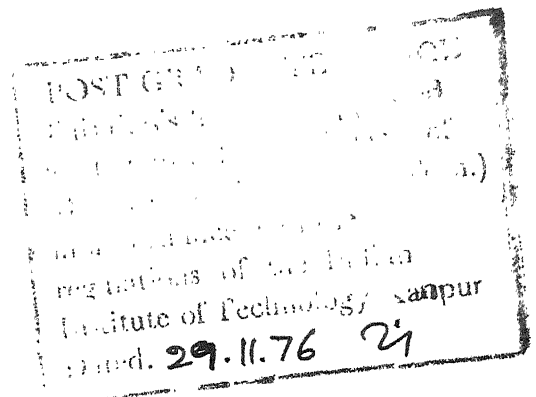
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CONTENTS

<u>Chapter</u>		<u>Page</u>
1.	INTRODUCTION	
1.1	Mineralogical Constitution and Benefication of Almora Magnesites	1
1.2	Effect of Impurities on the Quality of Magnesite Sinter	8
2.	STATEMENT OF THE PROBLEM	13
3.	EXPERIMENTAL PROCEDURE	15
3.1	Materials	15
3.2	Almora, Salem and South Korean Sintered Magnesites	16
3.3	Methods	17
3.3.1	Ball milling	17
3.3.2	Heavy liquid separation	19
3.3.3	Preparation of Almora magnesite, calcium carbonate compositions, pressing and sintering of pellets	20
3.3.4	Differential thermal analysis	22
3.3.5	X-ray powder diffraction studies	22
3.3.6	Infra-red spectroscopy	24
3.3.7	Mossbauer spectroscopy	24
4.	RESULTS AND DISCUSSION	26
4.1	Raw Almora Magnesite	26
4.1.1	X-ray diffraction	26

4.1.2	Differential thermal analysis	29
4.1.3	Infra-red spectra	32
4.1.4	Mossbauer spectra	33
4.1.5	Concluding remarks	35
4.1.6	Raw magnesite from Salem	35
4.2	Size Fractions of Almora Raw Magnesite	37
4.2.1	X-ray diffraction	37
4.2.2	Differential thermal analysis	40
4.3	Heavy Liquid Separation of Calcined Almora Magnesite	41
4.4	Sintered Magnesites of Almora, Salem and S. Korea	42
4.5	Grinding Characteristics of Almora and Salem Magnesites	44
4.6	Effect of Calcium Carbonate on Almora Magnesite Sintered at 1700°C	47
5.	CONCLUSIONS AND RECOMMENDATIONS	50
	REFERENCES	52

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I.1	Major Magnesite Deposits in India	2
I.2	Temperature of Initial Liquid Formation in Magnesites	11
III.1	Chemical Analyses of Almora and Salem Magnesites	15
III.2	Chemical Analyses of Almora, Salem and S. Korean Sintered Samples	17
III.3	Conditions of Grinding Almora and Salem Magnesites	18
III.4	Specific Gravities of Relevant Species	19
III.5	Instrument Parameters for X-ray Diffraction	23
IV.1	X-ray Diffraction Pattern of Raw Magnesites of Almora and Salem	27
IV.2	Mossbauer Spectrograph Characteristics of Raw and Sintered Almora Magnesite Iron Contents	34
IV.3	Variation in Calcite, Dolomite and Talc Abundances in Different Size Fractions	46
IV.4	Grinding Characteristics of Magnesites	46

LIST OF FIGURESFigure

- 4.1 D.T.A. pattern of raw Almora magnesite (unseparated)
- 4.2 Infra-red spectra of unseparated and -325 mesh fraction of Almora magnesite
- 4.3 Infra-red spectra of Salem and pure magnesites, calcite and dolomite
- 4.4 Mossbauer spectra of raw and sintered magnesites
- 4.5 X-ray diffraction pattern of different size fractions of Almora magnesite
- 4.6 D.T.A. pattern of raw Almora magnesite (-8 + 20 mesh) on 15 minutes grinding
- 4.7 D.T.A. pattern of raw Almora magnesite (-60 + 100 mesh)
- 4.8 D.T.A. pattern of raw Almora magnesite (-140 + 230 mesh) on 15 minutes grinding
- 4.9 D.T.A. pattern of raw Almora magnesite (-230 + 270 mesh) on 15 minutes grinding
- 4.10 D.T.A. pattern of raw Almora magnesite (-325 mesh) on 15 minutes grinding
- 4.11 X-ray diffraction pattern of Almora magnesite in the raw and calcined forms - light fractions
- 4.12 X-ray diffraction patterns of sintered S. Korean, Salem and Almora magnesites

- 4.13 D.T.A. patterns of Almora, Salem and S. Korean sintered samples
- 4.14 Semilog plot of % finer Vs. particle size (microns) of Almora magnesite
- 4.15 Semilog plot of % finer Vs. particle size (microns) of Salem magnesite
- 4.16 Log-log plot of % finer Vs. particle size of feed and product
- 4.17 X-ray diffraction pattern of Almora magnesite, calcium carbonate compositions sintered at 1700°C and cooled under different condition.

SYNOPSIS

Almora magnesite is studied to establish the minerals responsible for the iron oxide, lime and silica in this magnesite. The iron comes from breunnerite. The sharp endothermic peak observed at 735°C in the DTA pattern immediately following the decomposition of magnesite at 670°C is characteristic of breunnerite. Quadruple splitting and an isomer shift of 1.332 mm s^{-1} observed in the Mossbauer spectrum for this magnesite showed iron to be present in divalent state in a hexagonal structure which may be siderite or breunnerite. Since no siderite was detected in X-ray diffraction pattern, the Mossbauer results were interpreted that breunnerite is the mineral responsible for iron in Almora magnesite. The shoulder observed around 6.8 microns in the infra-red spectrum, near the magnesite peak at 7 microns, is tentatively attributed to the presence of iron in this sample.

In addition to dolomite and calcite reported earlier, huntite, a mixed carbonate of calcium and magnesium, $\text{CaMg}_3(\text{CO}_3)_4$ is also seen to be present in Almora magnesite. This mineral with its characteristic peaks at $d = 2.834(100)$, $2.44(60)$, $2.20(60)$, $1.986(80)$ and $1.769 \text{ \AA} (80)$ was detected in the X-ray powder diffraction pattern of Almora magnesite.

The DTA pattern of Almora magnesite is found to record a shoulder (at 500°C) to the intense magnesite peak at 670°C. This endotherm at 500°C is due to huntite, as quoted in literature. Other two peaks, one coinciding with the intense breunnerite peak and the other at about 840°C are also observed.

In order to pinpoint the presence of the carbonates and silicates and to elucidate the possibility of eliminating them, certain methods like size fractioning of ground material and heavy liquid separation of raw and calcined magnesite were studied. Results indicate that under the grinding conditions employed the size fractions have increasing talc content in the finer fractions. Calcite and dolomite concentrate in intermediate fractions.

X-ray and DTA studies on sintered samples of Almora, Salem and South Korea indicate that Almora sample has some amount of undecomposed magnesite and calcite. This suggests that Almora sample has been sintered at a lower temperature than the other two samples.

Studies on the effect of calcium carbonate addition to Almora magnesite showed that calcium oxide is not incorporated either in the periclase lattice or in the form of any silicate.

Mossbauer studies on sintered sample of Almora magnesite showed an assymmetric absorption peak with an isomer shift of 1.142 mm s^{-1} . No quadruple splitting was observed. These results are interpreted to conclude that iron in this sample is present in a cubic structure and a major portion of it is in divalent state with a smaller portion also existing in trivalent state. This suggests the presence of magnesiowustite which has iron in the divalent form and magnesioferrite which has iron in the trivalent form.

CHAPTER 1

INTRODUCTION

1.1 Mineralogical Constitution and Beneficiation of Almora Magnesites

There are two distinct varieties of magnesite deposits in India - the microcrystalline variety of Salem, Tamil Nadu, which originated from preexisting ultrabasic rocks^{2,3} and the crystalline magnesites of Kumaon range in Almora district of Uttar Pradesh, which originated through a process of replacement by the action of hydrothermal magnesian fluids on preexisting dolomites.¹ There are 44 million tonnes of magnesite reserves in Salem and about 27 million tonnes in Almora according to the official estimates. In 1973, about 1.933 lakh tonnes of magnesite was produced and 1.787 lakh tonnes were consumed, refractories industry taking a major share of 1.498 lakh tonnes. In 1974, the production of magnesite was stepped upto 2.658 lakh tonnes.⁵

Chemical analyses of magnesite deposits from several localities of Salem and Almora are given in Table 1.1. It is clear that these deposits exhibit extreme variation in their composition as summarized below:

<u>Constituent</u>	<u>Salem</u>	<u>Almora</u>
MgO	31.5 - 48%	40 - 45%
CaO	0.5 - 17%	0.1 - 5.1%
SiO ₂	0.7 - 12%	1 - 3.4%
Fe ₂ O ₃	0.08 - 1.10%	2.4 - 4.4%

Table 1.1 Major Magnesite Deposits in India

A. Salem District (Tamil Nadu)*

	<u>Location</u>	<u>SiO₂</u>	<u>Fe₂O₃</u>	<u>CaO</u>	<u>MgO</u>	<u>Ign. loss</u>
1.	Chalk hills (Northern area)	0.70	0.40	0.60	47.85	50.40
2.	Chalk hills (Southern area)	1.85	0.08	0.81	46.41	50.64
3.	Siranganur	1.69	0.16	1.20	45.46	51.54
4.	Kundamalai	2.40	0.56	17.32	31.51	48.14
5.	Pavittiram	1.02	0.47	8.69	39.36	49.62
6.	Kanjur-dasampatti	12.16	1.00	1.44	40.07	55.33
7.	Thevur	2.62	1.10	0.50	45.37	50.41
8.	Chettipatti	4.06	0.60	1.12	44.31	49.91

(* Source: Krishnan, M.S., GSI Mem., Vol. 80, 1951).

(Table 1.1 continued)

B. Almora District (Uttar Pradesh)*

	<u>Location</u>	<u>SiO₂</u>	<u>Fe₂O₃</u>	<u>CaO</u>	<u>MgO</u>	<u>Ign. loss</u>
1.	Agar-Girechchina	3.30	2.48	5.12	40.85	48.21
2.	Dewaldhar (I-II)	1.25	4.39	0.75	43.27	49.97
3.	Dewaldhar (III-VI)	1.12	2.64	0.65	44.58	50.12
4.	Harap	3.38	2.41	0.14	44.91	48.81

(* Source: Ref. 4 and Ref. 14).

In order to overcome the problems arising from such wide variability, selective mining of magnesite is generally resorted to. However, selective consumption of magnesite of only superior grade by the refractory industry is likely to exhaust Indian resources of magnesites in about two decades. Therefore suitable measures are to be taken to utilize the ores containing high silica, lime and other impurities by beneficiation and careful mining. In this context, the exploitation of Almora magnesite may ease the situation.

ISI specifies minimum MgO of 85% and the maximum SiO_2 and CaO contents of 4.5% and 2.5% respectively for the dead burnt magnesite and for magnesite brick. In the case of Salem magnesite silica is mainly present as quartz whereas in Almora variety it is present as talc. Methods of removal of impurities by hand are costly and difficult, particularly in the case of Almora magnesites.⁴ The association of talc is very intimate everywhere in Almora and must have been the reaction product of the mineralizing fluid with the available silica. The talc, particularly in the Dewaldhar deposit, is rather very fine-grained and associated with some clay-like material. Here it is distributed evenly as triangular inclusions in between interlocking carbonate grains. On the whole, the complete removal of talcose impurities is not easily feasible.¹²

Beneficiation tests were carried out at the Indian Bureau of Mines⁶ on two samples of low grade magnesite from Salem assaying 41.88% MgO, 0.86% CaO, 0.24% Fe₂O₃, 0.10% Al₂O₃, 12.24% acid insolubles and 45.80% L.O.I. for one and 46.60% MgO, 1.1% CaO, 0.33% FeO, 0.13% Al₂O₃, 2.10% SiO₂ and 49.35% L.O.I. for the other. Their results indicated that magnesite concentrates of suitable grade could be obtained assaying 45.36% MgO and 1.93% SiO₂ with an overall MgO recovery of 85.67% in the case of the first sample and concentrates assaying 47.17% MgO and 1.1% SiO₂ with an overall MgO recovery of 95.08% in the second sample.

From a study of the published literature on Indian magnesites and their beneficiation two points become very clear. One, that the magnesite ore resources in our country are vast but a major fraction of the resources need beneficiation before they are exploited.^{4,7,8} Two, that the studies on beneficiation of the ores or their exploitation by suitable adjustment of the proportions of different impurities have been limited.^{6,9,10} Both the methods of exploitation are based, for their success, on a thorough knowledge of the sources of the various impurity oxides in the impure magnesites and of the phase relationships between these oxides at the working temperatures and environments.

Based on X-ray and DTA studies, Rao¹¹ reported that in the sample of Almora magnesite (from Agar-Girechchina) the silica is contributed mostly by talc and to a small extent by chlorite and the lime content of the magnesite is due to dolomite and not calcite. Although some hematite was observed most of the iron appeared to be in solid solution as seen by the exothermic peak at 700°C in DTA study.

Banerjee and Sircar in their studies on Almora magnesites,^{12,13} reported that the hand specimens of Agar-Girechchina in Almora revealed certain white carbonate grains which may be calcite while hand specimens of Harap deposits did not appear to contain any dolomite. Microscopic studies revealed that while Agar-Girechchina sample showed dolomite along with evidences of incomplete mineralisation of preexisting dolomites, the dolomite as a lime impurity is rather rare in magnesites from Lahore Valley and is less frequent in the Dewaldhar deposits, especially in blocks I to VI. Talc is an invariable impurity occurring in the form of stringers, streaks, veins and massive pockets. While in Agar-Girechchina it favours localized concentration, in the Lahore Valley (Pungar deposits) talc is rather uniformly dispersed. In Dewaldhar talc is rather very fine-grained, grey coloured and is distributed evenly as triangular inclusions in between carbonate grains.

Increase in the refractive index of the magnesite grains suggested a limited solution of siderite with magnesite.

X-ray study showed that next to magnesite, dolomite is usually the most abundant. Calcite and its polymorph ²aragonite occurred in large proportions in the sample from Harap and to much lesser extent in samples from Dewaldhar and Agar Girechchina. Talc was found in all the samples while quartz is identified only in Dewaldhar.

A minor shifting or broadening of the magnesite lines was attributed to the siderite solid solution in magnesite.

Their DTA results also confirmed the presence of calcite in the samples from Dewaldhar Blocks III to VI and Harap. Therefore the authors state that the calcium content of Almora magnesites was not necessarily due to dolomite only, as suggested by Rao et al.,¹¹ although dolomite was found to be the major source for calcium in majority of the samples. A thermogram of talc separated from the Harap sample showed a shallow endothermic peak at 1000°C, although they did not find this peak in the unseparated sample.

In a study of chemical and magnetic properties of Almora magnesites, Banerjee et al.¹⁴ reported an evidence for siderite being in solid solution with magnesite since these magnesites indicated a paramagnetic susceptibility

due to ferrous ion. They considered this observation to infer the 'breunnerite' nature of the Almora magnesites in the absence of sufficient evidence in X-ray, DTA and microscopic studies excepting an observed increase in refractive indices assumed to be indicating some solid solution of siderite in magnesite.

1.2 Effect of Impurities on the Quality of Magnesite Sinter

Rao et al¹⁰ studied the effect of lime/silica ratio at different silica levels on the mineralogical constitution and refractory properties of the magnesite sintered at 1500-1680°C for 3 hrs using Salem magnesite as the starting material. They found forsterite formation up to a CaO/SiO_2 ratio of 0.80. Up to this ratio monticellite was the only silicate of calcium observed and its amount increased with the silica content for CaO/SiO_2 ratio greater than 0.38. Merwinite appeared in compositions with CaO/SiO_2 greater than 1.15 at the expense of forsterite which was no longer observed. The amount of monticellite and merwinite increased with silica content. As the CaO/SiO_2 ratio was raised to 1.53, monticellite was no longer observed and instead β -dicalcium silicate and merwinite constituted the silicate phases. For compositions ^{with the ratio} greater than 2 only β -dicalcium silicate was formed. Highest refractoriness underload

values were obtained with this silicate phase. At 5% silica level, best refractoriness underload values were reported for CaO/SiO_2 molar ratios below 0.38 and above 2.0. However, the possibility of the refractory, in service, absorbing lime from the furnace atmosphere led them to suggest a brick composition with CaO/SiO_2 ratio greater than 2.0 and a minimum silica content possible so that in the event of lime absorption only tricalcium silicate, which is a highly refractory phase, will form. At the maximum levels of lime and silica permitted by ISI, the CaO/SiO_2 ratio is 0.487. At this level the authors found that even if the silica content is increased to 10% there is no significant drop in refractoriness underload. Keeping in view the possible lime absorption in steel plants, however, the silica content should be kept to a minimum so as to avoid excessive formation of liquid silicates.

Kreik and Segal¹⁵ found that the strength of magnesite bricks is, to a large extent, related to the type and amount of silicates present and to the temperature of initial liquid formation. They found that the effect of iron oxide additions on the strength of magnesites at high temperatures was small when the bonding silicates are forsterite, monticellite or merwinite but is greater when the bonding silicate is dicalcium silicate. Thus the

lowering of strength due to presence of iron oxide becomes most pronounced at CaO/SiO_2 levels greater than 2. C_2S bonded bricks containing low amounts of iron oxide are stronger and have the ability to deform (without rupture) more than can direct-bonded or normal chrome-magnesites.

Thus the iron oxide present in Almora magnesites becomes a very crucial impurity which can mar the superior properties of C_2S bonded bricks. The temperatures of initial liquid formation in magnesites for the various phase fields are presented in Table I.2.

Among the R_2O_3 oxides namely Fe_2O_3 , Al_2O_3 , Cr_2O_3 and B_2O_3 the latter is the most deleterious and Fe_2O_3 is the least deleterious in its effect on lowering the strength of magnesite refractories. The reason for the Fe_2O_3 resulting in small decrease in strength is the result of its ability to enter into solid solution in the periclase phase as FeO thus reducing the effective quantity of Fe_2O_3 to increase the flux content. All the same, the possibility of its exsolution from the periclase structure is governed by change in oxygen partial pressure and temperature.¹⁶ In the service the bricks are exposed to the changes in oxygen partial pressure and temperature to varying degrees depending on the part of the furnace or vessel where it is employed.

Table I.2 Temperature of Initial Liquid Formation in
Magnesites¹⁵

Phases present	Temperature of initial liquid formation, °C
MgO, M ₂ S	1850
MgO, M ₂ S, CMS	1502
MgO, CMS, C ₃ MS ₂	1498
MgO, C ₃ MS ₂ , C ₂ S	1575
MgO, C ₂ S, C ₃ S	+2000
MgO, M ₂ S, MA, MF	1570-1580
MgO, CMS, MA, MF	1410
MgO, C ₃ MS ₂ , MA, MF	1380
MgO, C ₂ S, MA, MF	1380
MgO, C ₂ S, MA, C ₄ AF	1290

C - CaO; M - MgO; S - SiO₂, A - Al₂O₃ and F - Fe₂O₃.

Thus the magnesite bricks made out of low iron high CaO/
SiO₂ ratio compositions seem to claim application in places
like open-hearth furnace roofs where the ability of the
bricks to deform and good high temperature strengths are
important requirements.

CHAPTER 2

STATEMENT OF THE PROBLEM

Salem magnesite has been the major source till now for meeting the supply of magnesite to refractories industry. Therefore most of the earlier work was concerned with the utilisation of this particular magnesite. The extensive magnesite deposits of Almora in U.P., although comparatively impure, are important due to their proximity to the steel plants. These have not been studied very thoroughly as yet. Their exploitation by the refractory industry can commence only after suitable methods of beneficiation are developed. For this purpose, a thorough knowledge of their mineralogical constitution is essential. While a number of mineralogical studies have been carried out on Almora magnesite, the picture remains far from clear because of the great variability of the various deposits. Further, considerable disagreement exists in the literature regarding the minerals responsible for major impurities namely, silica, lime and iron oxide in these magnesites.

The present work deals with Almora magnesite and aims at identifying the associated carbonates and silicates in them. An attempt has also been made here to concentrate the impurities to obtain magnesite rich

fractions. With this aim in mind various methods like size fractioning after grinding, heavy liquid separation, and controlled calcination followed by heavy liquid separation were studied.

Mineralogical constitution after heat treatment at various temperatures has been studied since magnesite is invariably used **in** the dead burnt or sintered form. The results of this phase of the study are compared with the mineralogical constitution of sintered magnesites of South Korea, Salem and Almora procured from the industry. An attempt has also been made to study the effect of varying the lime/silica ratio of the magnesite on the mineralogical constitution of the sinters calcined at 1700°C. X-ray diffraction, differential thermal analysis, Mossbauer spectroscopy and infrared spectroscopy have been used as the chief analytical tools.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Materials

The raw magnesite of Almora studied was grayish white in colour and was in the form of lumps around 20 cms size. The Salem magnesite samples were relatively smaller in size (between 30 and 40 nm) and were almost pure white in colour. The chemical analyses of both these magnesites is given in Table III.1.

Table III.1 Chemical Analyses of Almora and Salem Magnesites

	Almora magnesite		Salem magnesite	
	Analysis 1	Analysis 2	Analysis 1	Analysis 2
MgO	46.75	47.10	44.63	45.62
CaO	1.26	1.59	1.15	1.62
Al ₂ O ₃	Nil	0.41	Nil	0.20
Fe ₂ O ₃	2.20	3.45	0.32	0.50
SiO ₂	0.20	0.27	4.89	4.18
L.O.I.	49.70	50.10	48.35	48.65

(Chemical Analysis by Analytical Chemist, Department of Metallurgy, I.I.T./Kanpur).

The two analyses of a given sample show a reasonably good agreement. The amount of the various constituents detected here fall within the range reported by other investigators. An important difference between the two sources of magnesite appears to be high Fe_2O_3 in Almora and high silica in Salem magnesite. It may be pointed out that some deposits of Almora are reported to have high lime. Such large lime contents are undesirable from a refractory standpoint. The larger CaO content can be traced to the genesis of Almora magnesites.

3.2 Almora, Salem and South Korean Sintered Magnesites

The sintered samples of Almora and S. Korea studied in the present investigation were in the form of grains used in the fettling and preparation of open-hearth furnace bottoms. The sintered Salem magnesite used in the present study was obtained by crushing a typical magnesite brick used in the steel plants. The chemical analyses of sintered magnesites from Almora and S. Korea are given in Table III.2 which may be compared with the ISI specifications listed there in.

Table III.2 Chemical Analyses of Almora, and
S. Korean Sintered Samples

	Almora sintered sample (%)	S.Korean sintered sample (%)	ISI specification (%)
MgO	87.32	90.10	85% min.
CaO	3.21	2.30	2.5% max.
Fe ₂ O ₃	5.00	1.10	-
Al ₂ O ₃	1.80	1.70	-
SiO ₂	2.00	3.50	4.5% max.
L.O.I.	0.5	1.25	-

3.3 Methods

The various experimental methods employed in the present work together with the equipment used are described below.

3.3.1 Ball milling

A laboratory ball mill of Ohio ^{Kilns,} Inc., U.S.A. was used to grind Almora and Salem magnesites. Typical grinding conditions employed are summarised in Table III.3.

Table III.3 Conditions of Grinding Almora and Salem
Magnesites

	Almora Magnesite	Salem Magnesite
Wt. of material	300 gms	233 gms
Wt. of balls taken	3x300 = 900 gms	3x233 = 699 gms
Speed	50 r.p.m.	50 r.p.m.
Duration of grinding	15 min.	15 min.

For the study of grinding characteristics the conditions of grinding adopted for Salem magnesite and Almora magnesite are identical except for the difference in the weight of the material taken.

The ground materials are separated into different size fractions using ASTM sieves and Fisher-Wheeler sieve shaker with 20 lb. maximum load capacity and the motor speed adjusted to 600 r.p.m. The shaker was operated for 20 min. A tendency for the finer fractions to globulate and therefore not get separated properly was noticed. This may be due to a moisture pick up by such fine fractions. In those cases special care was taken to break up the globules and continue the sieving manually till no further material passes through.

3.3.2 Heavy liquid separation

The specific gravities of the constituent minerals in raw and calcined magnesites are given in Table III.4.

Table III.4 Specific Gravities of Relevant Species

Species	Specific gravities
Magnesite	2.98 - 3.02
Calcite	2.71
Dolomite	2.84 - 2.86
Huntite	2.70
Siderite	3.95 - 3.97
Talc	2.58 - 2.83
Quartz	2.65
Monticellite	3.08 - 3.27
Merwinite	3.15
Forsterite	3.22
Magnesioferrite	4.60
Periclase	3.56

In order to concentrate the heavy species from the lighter ones as an aid to the determination of mineral

constitution of raw and calcined magnesites, heavy liquid separation was carried out with bromoform medium (specific gravity 2.87). For this purpose about 2 gms of the material was added each time to the tube containing bromoform and was allowed to descend slowly through the orifice in the inner tube. The choking at the orifice was prevented by slight tapping with the finger. The final settling was accomplished by centrifuging for about 10 min. at a speed of 7500 r.p.m. using a Sorval Angle Centrifuge Type XL. After centrifuging the inner tube containing light fractions was emptied of its contents into a filter paper in a funnel which was then washed and dried.

3.3.3 Preparation of Almora magnesite, calcium carbonate compositions; pressing and sintering of pellets

The starting materials include Almora magnesite ground in Ball mill and analytical reagent grade calcium carbonate. The compositions chosen for the study include 0%, 1%, 2%, 4%, 8%, 12%, 16% and 20% by weight of calcium carbonate approximately. The preparation of a 4% calcium carbonate, Almora magnesite pellet is described below, for providing an example.

1. Powder preparation: 9.6003 gms of Almora magnesite and 0.3996 gms of calcium carbonate were taken in an Agate mortar and wet mixed in acetone thoroughly. The material

was then transferred into an alumina crucible and calcined in a silicon carbide globar furnace at 800°C for 3 hrs. Precalcination before sintering of the material in the form of pellets, was felt necessary for preventing cracking of the pellets during sintering due to evolution of carbon dioxide

2. Pressing of pellets: The calcined material was a loose powder and therefore did not necessitate any elaborate grinding. The material was mixed well to obtain homogeneity. Pellets were pressed using Carver hydraulic press in a 3/8" dia. steel die under a pressure of 13,000 psi. The pellets did not show any defects like cracks or laminations. The dimensions of the pellets, so obtained, for the various compositions were measured with a micrometer screw gauge with a least count of 0.01 mm. The pellets were then transferred to a desiccator.

For compositions containing, 1%, 2% and 4% calcium carbonate the procedure for preparation of pellets was identical. The compositions containing, 0%, 8%, 12%, 16% and 20% calcium carbonate were pressed into pellets in a 1/2" dia. steel die under 13000 psi pressure.

3. Sintering of pellets: The sintering of pellets was carried out in a gas fired furnace at 1700°C for 1 hr. The

rate of heating was 60°C/hr up to 1000°C and 100°C/hr from 1000°C to 1700°C. The pellets were cooled along with the furnace at its natural cooling rate over 48 hrs duration.

Another batch of pellets made from compositions containing 1%, 2% and 4% calcium carbonate were fired in a platinum resistance furnace at approximately 1700°C; these pellets were cooled at a faster rate than the ones sintered in gas fired furnace.

3.3.4 Differential thermal analysis

Differential thermal analyses were carried out on Du pont 900 analyzer fitted with 1200°C cell assembly using Pt-Pt 10% Rh thermocouples and with α -Al₂O₃ as the reference material. The heating and cooling rates were maintained at 10°C/min. The cooling curves were obtained to establish the reversibility or otherwise of the reactions. Some of the samples have been investigated over a number of heating/cooling cycles. In some cases the heating was interrupted at selected temperatures in order to elucidate the reactions taking place.

3.3.5 X-ray powder diffraction studies

X-ray powder diffraction work was carried out on General Electric XRD-36 Diffractometer. The conditions of diffraction and instrument parameters used for the different samples are shown in Table III.5.

Table III.5 Instrument Parameters for X-ray Diffraction

Instrument parameter	For raw Almora sample, sintered samples, Almora magnesites-CaCO ₃ fired pellets	Size fractions and heavy liquid separated samples of Almora magnesite
Radiation	CuK _α	CoK _α
Filter	Ni	Iron
Detector slit	0.05°	0.2°
Beam slit	3°	3°
Soller slit for incident beam	Medium resolution	Medium resolution
Soller slit for diffracted beam	Medium resolution	Medium resolution
Voltage to X-ray tube	35 KV	30 KV
Current in X-ray tube	20 mA	8 mA
Scanning speed	2° 2θ/min.	2° 2θ/min.
Chart speed	2"/min	1"/min
Intensity range (for full scale deflection of pen)	500 cps & 200 cps	500 cps
Time constant	4 sec.	4 sec.

The intensity range for the full scaled deflection of pen was 500 cps uniformly for all the samples. The sintered pellets of Almora magnesite calcium carbonate compositions

were scanned with 200 cps intensity range for the full scaled deflection of the pen also in order to elucidate the silicate peaks obtained in a narrow range.

3.3.6 Infra-red spectroscopy

Perkin-Elmer 137 Spectrometer was used with sodium chloride prism to study infra-red characteristics of various magnesite samples from 700 to 4000 cm^{-1} frequency range corresponding to wavelengths of 3 to 15 microns. A few milligrams of the material of -325 mesh was mixed with KBr and pressed into a pellet form for the infra-red study. In order to elucidate the constituent minerals in the magnesite, infrared spectra of high purity specimens of magnesite, calcite and dolomite supplied by Tempress Inc., (U.S.A.) were also obtained. For the purposes of comparison infra-red spectrum of Salem magnesite was also run. As far as Almora magnesite is concerned, both the representative sample as well as the finest fraction (-325 mesh) obtained in the grinding test were examined in the infra-red study.

3.3.7 Mossbauer spectroscopy

Iron is a very common impurity in magnesites. The valency state of this species in the raw and sintered magnesites can provide important information about the

manner in which iron is present in these materials. This information is most effectively provided by a study of these materials in the raw and sintered conditions by the Mossbauer spectroscopy. For this purpose the sample is taken in the -325 mesh size and placed in a thin layer in a copper ring. The sample is held in place by scotch tape. The sample density is 70 mgm/sq cm. The Mossbauer spectrometer used was developed at I.I.T./Kanpur and produced by Encardiorite, Lucknow. This is used in conjunction with a 512 Multichannel Analyzer supplied by Electronics Corporation of India Ltd. The radiation source is Co^{57} embedded in stainless steel. The total number of counts, at each position, employed for the different samples is as follows:

Raw Almora : 120,000

Raw Salem : 90,000

Sintered Almora : 60,000.

These data are plotted as a function of the number of channels or, in other words, velocity.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Raw Almora Magnesite4.1.1 X-ray diffraction

The X-ray diffraction pattern of raw Almora magnesite is presented in Table IV.1 together with that of a standard X-ray pattern (ASTM). As expected magnesite is the dominant mineral, evidenced by the fact that all major lines in our pattern ^{are} accounted for by magnesite lines. It may, however, be noticed that the d-spacings of many of the reflection in the sample are slightly (about 0.002 \AA) shifted compared to the corresponding lines in the standard pattern. This decrease in the d-spacings can be ^{accounted} ~~attributed~~ for if the iron present in Almora magnesite enters the magnesite lattice i.e. if Fe^{2+} ion (radius = 0.68 \AA) replaces Mg^{2+} ion (radius = 0.74 \AA). A magnesite in which Fe^{2+} partially substitutes for Mg^{2+} is called breunnerite. Breunnerite can also be visualised as arising from solid solution of siderite (FeCO_3) in magnesite. The large amount of iron present in Almora magnesite (Table III.1) makes the mixture of breunnerite in this magnesite quite plausible.

Table IV.1 X-ray Diffraction Pattern of Raw Magnesites of Almora and Salem

Raw magnesite of Almora		Raw magnesite of Salem		Pure magnesite		Minerals with their characteristics peaks at this d value
d	I	d	I	d	I	
9.300	2					T
4.260	2					Q
4.371	1-2					
3.839	6					C
3.386	7					
3.288	23					V
3.030	49	3.030	4			C
2.855	16	2.864	2			D
2.833	14	2.846	2			H
		2.825	2			
2.724	>50	2.740	>60	2.740	100	V
2.499	30	2.503	13	2.503	18	T
2.396	1-2					
2.313	5	2.316	6	2.318	4	
2.174	7-8					D, C, H
2.097	36	2.102	48	2.100	45	V
2.004	2					D
1.934	11	1.940	15	1.939	12	
1.879	2-3	1.886	2			
1.767	2-3	1.770	5	1.769	4	H
1.697	50	1.703	40	1.697	35	
1.534	1-2					
1.507	3-4	1.509	5	1.510	4	
1.485	3-4	1.485	7	1.488	6	
1.405	4	1.407	6	1.426	4	
1.369	17			1.371	4	
1.351	6	1.355	8	1.354	8	
1.336	5-6	1.338	12	1.338	8	
1.250	11	1.251	4	1.252	4	
1.179	2-3	1.179	4			
1.101	2-3					
1.098	2-3					

T Talc ; Q Quartz ; V Vaterite ; D Dolomite ;
H Humate

The diffraction lines in Table IV.1 not accounted for by magnesite were made use of to identify the major associated minerals. This is indicated by **assigning these** lines to the various minerals in the table. For example, it is clear that calcite is the dominant impurity as evidenced from reflections (3.86(12), 3.04(100), 2.50(14), 2.29(18), 2.095(18), 1.913(17), 1.875(17), 1.525 Å⁰(5)). Calcium carbonate appears to be present in another polymorphic form namely vaterite with the lines at 3.30(100), 2.73(100), 2.06(100). In addition to these two, presence of dolomite and huntite¹⁸ has also been established. Dolomite has its characteristic peaks at $d = 2.89(100)$, $2.19(30)$, $2.015(15)$, $1.79(30)$ and $1.781(30)$. While huntite has its peaks at $2.84(100)$, $2.44(60)$, $2.20(60)$, $1.986(80)$, $1.769(80)$, $1.480(60)$. It may be pointed out that both these minerals are mixed magnesium calcium carbonates with the formula for dolomite $Mg, Ca(CO_3)_2$ while huntite has the formula $Mg_3Ca(CO_3)_4$. It may be emphasized that in none of the earlier studies on Almora magnesite huntite has been reported. However, considering the fact that Almora magnesite arises due to the action of the magnesian solutions on calcareous rocks the presence of huntite should not at all be surprising. Since huntite has not so far been reported in this material it would be necessary to find other evidence to corroborate

the results of X-ray study. This has been provided ^{by} in the DTA study as discussed in the next section.

The next mineral in importance in Almora magnesite seems to be Talc, $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. The clear evidence for this consists ^{of} in the diffraction lines at 9.3(48), 4.58(64), 3.13(40), 2.49(100), 1.53 Å (64). Talc, calcite and dolomite have been reported as associated impurities by Banerjee et al.¹² and Rao¹¹.

It may be noticed in Table IV.1 that some lines remain unaccounted for by any of the minerals mentioned above. It has not been possible to assign these lines to any likely minerals at present. It may however, be noted that such lines have very low intensity implying that they are due to some minor species.

4.1.2 Differential thermal analysis

The differential thermal pattern for raw Almora magnesite is presented in Figure 4.1. The intense endothermic peak around 670°C corresponds to the decomposition of the magnesite mineral. In a pure magnesite mineral, with the completion of the decomposition event the pattern returns to the base line.¹⁹ However, in the present case a sharp exotherm at 735°C immediately following the endotherm was clearly noticed. This is characteristic of breunnerite¹⁹

(a ferroan magnesite) in which the decomposition of the carbonate is followed by the oxidation of the iron. In the present case, the decomposition peak attains its maximum at a temperature (670°C) relatively higher than for a pure magnesite (625°C) and also somewhat higher than the particular sample of breunnerite, $(\text{Mg}_{2.45}\text{Fe}_{0.55})\text{CO}_3$, reported by Kloss¹⁹ (650°C). The higher temperature in the present case may indicate the presence of ~~larger~~ ^{higher} iron content compared to that quoted by Kloss. By the same token, the position of the exothermic peak is shifted to higher temperature than that shown by Kloss¹⁹ ~~to~~ ^{for} his breunnerite. The magnitude of the exothermic peak in the present case also appears to be greater than that of the sample quoted by Kloss.¹⁹ All these factors appear to point to a ~~larger~~ ^{different} concentration of iron than for the sample reported by Kloss.¹⁹ This is consistent with the chemical analysis of Alnora magnesite (Table III.1) which shows a considerable iron content. While DTA evidence for breunnerite appears unequivocal the shift of X-ray diffraction lines was only slight. This may perhaps be due to the very small difference in ionic radii of Fe^{2+} and Mg^{2+} ions in the breunnerite lattice.

Another striking feature is the presence of a clear shoulder to the major endothermic peak on the low temperature side at the onset of decomposition. This

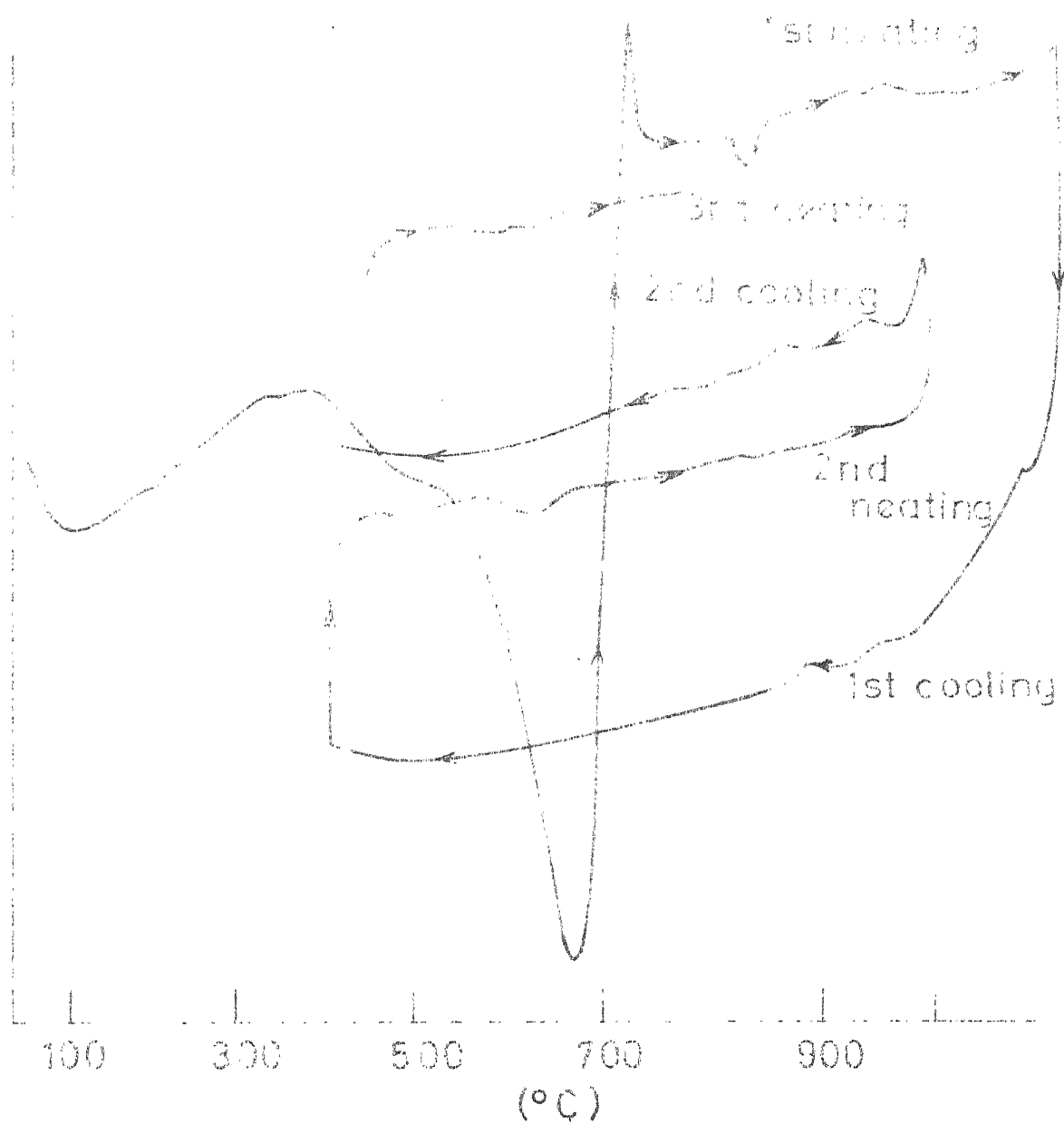


FIG.4.1 D.T.A. PATTERN OF RAW ALMORA MAGNESITE (UNSEPARATED)

should^{er} has its maximum around 500°C. This corresponds to the endothermic peak for huntite quoted in the literature.¹⁹ The typical pattern of huntite has an intense endothermic event following this shoulder and also a similar peak of comparable intensity around 800°C. In the present case the first major endothermic event following the shoulder overlaps that for breunnerite and the second endothermic peak is noticed in the 840°C region.

The endothermic peak in the 840°C region is broad and has maxima at three places indicative of the overlap of the peaks for dolomite and calcite in this region. Dolomite normally is characterized by two endothermic peaks and in the present case the other endothermic peak precedes the composite peak described.

The broad and shallow endothermic peak in the 1000°C region can be relegated to the dehydroxylation of talc. Since the endotherm attributed to talc is not sufficiently distinctive it would be useful to concentrate the talc content of Almora magnesite in some fractions. This is discussed further in subsequent sections.

The Almora magnesite sample has been heated to 1120°C and allowed to cool at the rate of 10°C/min down to 450°C. This process of heating and cooling has been continued for two more cycles. The corresponding cooling

and heating curves are also included in Figure 4.1. The main events noticed during cooling are two exothermic peaks occurring around 960°C and 880°C. The sharpness of these peaks improves with repeated cycling. These effects are tentatively attributed to the exsolution of iron and perhaps calcium oxides from the periclase lattice. In the second cycle heating a broad endotherm around 650°C was seen which splits into two smaller endotherms in the third heating in the same temperature range, one around 605°C and the other around 660°C. These endotherms may be due to the oxidation of the iron oxide obtained by the decomposition of magnesio-wustite or magnesioferrite during cooling or alternately they represent the curie temperature of the iron oxide phases α -Fe₂O₃ (675°C) or γ -Fe₂O₃ (640°C).

4.1.3 Infra-red spectra

The infra-red spectra of a representative sample of Almora magnesite and that of the finest fraction (-325 mesh) obtained on grinding are shown in Figure 4.2. For the purposes of comparison, spectra of pure magnesite, calcite and dolomite are shown in Figure 4.3. The three intense peaks around 7 microns, 11.3 microns, 13.5 microns tally with those for pure magnesite. However, in the Almora representative sample, a split in the peak in the

7 micron range with its shoulder around 6.8 microns is clearly evidenced. This possibly is due to the ferroan magnesite (breunnerite) in the Almora sample. In the pattern for the finest fraction of the Almora sample (-325 mesh) an additional peak is noticed in the 10 micron range which corresponds to that for silicates such as talc.

4.1.4 Mossbauer spectra

The Mossbauer spectrum of raw Almora magnesite is given in Figure 4.4. There are four symmetric fingers as the prominent feature of the spectrum indicating quadrupole splitting. This suggests that iron is present in a configuration which lacks axial symmetry²³ of electric field gradient. This is understandable because of the hexagonal structure of the magnesite. The line width (full width at half height), quadrupole splitting and isomer shift were calculated and are given in Table IV.2. The isomer shift of 1.332 mm s^{-1} indicates that iron is present in the divalent state in the raw magnesite. This provides a clear cut evidence for incorporation of iron in a divalent state in Almora magnesite. Since siderite has not been detected in the X-ray study, the above results can be interpreted only by the presence of breunnerite in Almora magnesite.

Table IV.2 Mossbauer Spectrograph Characteristics of Raw
And Sintered Almora Magnesite Iron Contents

	Iron in Raw Almora Magnesite	Iron in Almora Sintered Magnesite
	mm/sec.	mm/sec
Line width (Full width at half-height)	0.4192	0.6479
Isomer shift	1.332	1.142
Quadruple splitting	1.9057	-

4.1.5 Concluding remarks

The X-ray, DTA, infra-red and Mossbauer studies clearly establish that raw Almora magnesite consists predominantly of breunnerite. The presence of huntite is clearly established. Calcite, dolomite and talc are the important associated minerals. It is necessary to devise some careful experiments to pinpoint the presence of these associated minerals and their possible separation. These aspects are discussed in the subsequent sections.

Though Almora magnesite has been studied in some detail by Banerjee and coworkers¹²⁻¹⁴ and Rao¹¹ it is interesting to note that they have not detected ~~clear-cut evidence either for breunnerite or for~~ huntite in their studies.

4.1.6 Raw magnesite from Salem

As already indicated in Table III.1 magnesite deposits of Salem are relatively more siliceous (SiO_2 about 4%) as compared to the Almora magnesite (SiO_2 about 0.2%). Further, Salem magnesite has very low iron content (0.3-0.5%) while the same is up to 3.5% in the Almora samples. X-ray diffraction pattern of Salem magnesite is given in Table IV.1. X-ray diffraction analysis of the Salem magnesite has revealed the occurrence of calcite and dolomite in

association with the dominant magnesite mineral. Although the chemical analyses indicated the presence of silica, no characteristic lines for quartz could be evidenced in the X-ray diffraction pattern. This might be due to several possibilities. The quartz might be present but below the detectable level with X-ray diffraction. The other possibility might be that the free silica is present in a cryptocrystalline form. It also is possible that the silica is present in a combined form as a silicate. It may be pointed out that the X-ray pattern indicated the presence of two reflections at $d = 1.405$ and 1.176 \AA which may be due to pyroxenes. This is plausible since pyroxenes generally occur in ultrabasic rocks of the type that are the host rocks for Salem magnesite.

The infra-red spectrum of Salem magnesite is shown in Figure 4.3 together with those of pure magnesite, calcite and dolomite. In addition to the absorption bands characteristic of magnesite, other bands are observed at about 10 and 12.6 microns. Both these appear to be due to SiO_2 or silicates.

Attempts to obtain Mossbauer spectrum of Salem magnesite resulted in the absence of any Mossbauer absorption peaks. This is indicated in Figure 4.4. Therefore iron seems to be nearly absent in Salem magnesite

consistent with the chemical analysis given in Table III.1.

4.2 Size Fractions of Almora Raw Magnesite

In order to examine whether some of the associated minerals in Almora magnesite appear predominantly in any particular size fraction, magnesite, after grinding in a ball mill for 15 min., has been separated into the following size fractions: $-3\frac{1}{2} + 8$, $-8 + 20$, $-60 + 100$, $-140 + 230$ and $-230 + 270$ mesh sizes. The different size fractions have been studied by X-ray diffraction and DTA methods.

4.2.1 X-ray diffraction

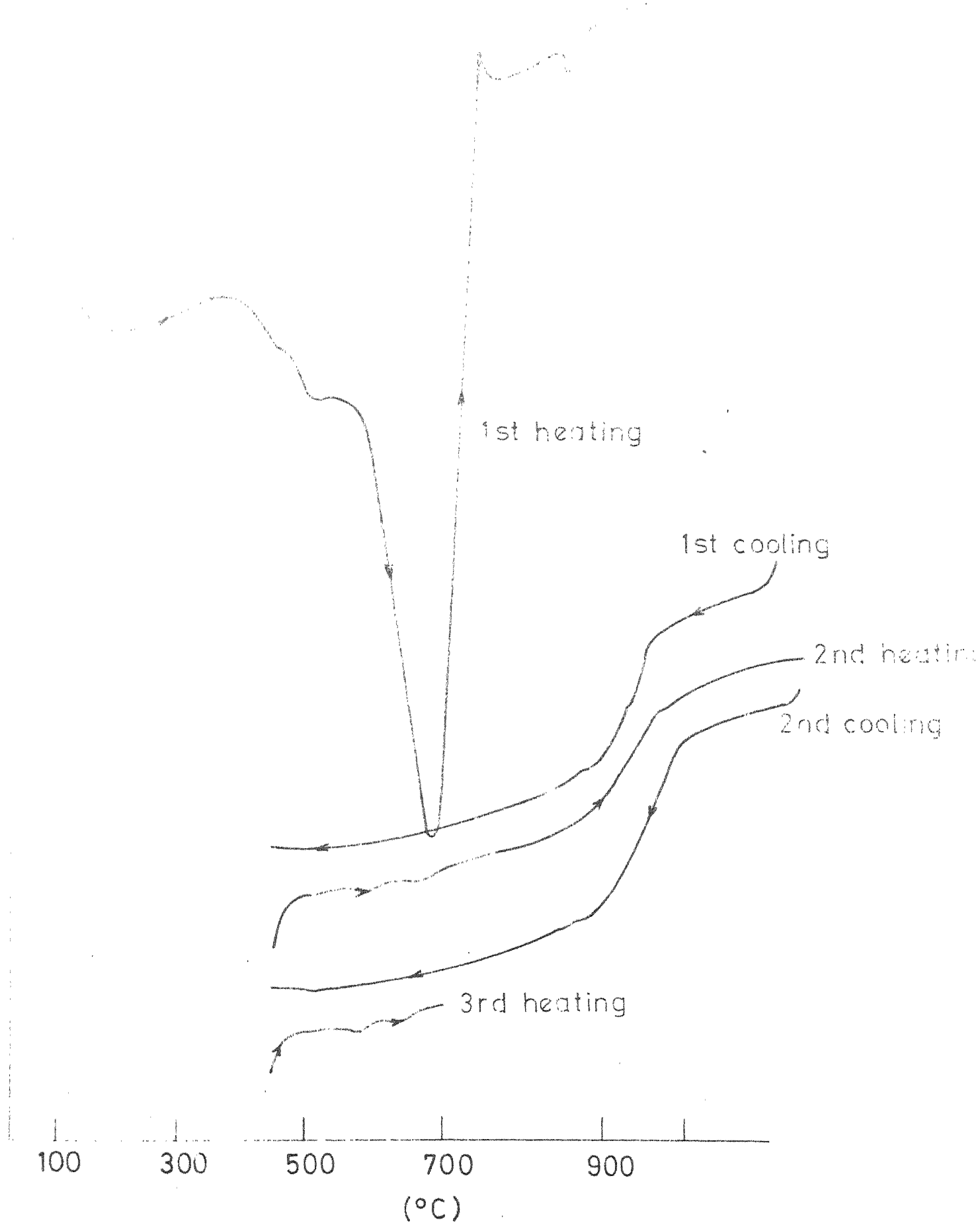
Basically the X-ray diffraction pattern of the different size fractions agree well with that of the composite sample. The main difference noticed has been in the relative impurity contents namely calcite, dolomite and talc as a function of particle size. A semiquantitative estimate of the abundance of these impurities may be obtained by noting the relative intensities of these minerals compared to that of a magnesite peak. These ratios are given in Table IV.3 which shows that the proportion of talc increases with the fineness of the material, being present to the maximum extent in the $-230 + 270$ mesh

fraction. The proportions of calcite and dolomite in Almera magnesite reach their maxima in size fraction -140 + 230 mesh and thereafter decrease. The above trends can be explained on the basis of the relative hardness of these minerals. For example, the hardness on Moh's scale of talc is 1, calcite 3, dolomite 3.5-4 and magnesite 3.5-4.5. Therefore the softest material, namely talc, gets concentrated in the finest fractions. Materials with intermediate hardness, namely calcite and dolomite, appear to predominate the intermediate fractions, thereby indicating their greater resistance to grinding than that of talc. As discussed in a later section these data may be made use of to produce magnesites containing less silica or less lime by eliminating the appropriate fine fractions.

An interesting behaviour has been observed in respect of the X-ray diffraction peak of magnesite at $d = 1.37 \text{ \AA}$ (Figure 4.5). The intensity of this peak increases gradually from a minimum in the coarse fractions to a maximum in the -140 + 230 mesh size. In the finer fractions the intensity again decreases. No explanation is available for this behaviour at present.

4.2.2 Differential thermal analyses

The differential thermal analyses data of different size fraction are presented in Figure 4.6 to Figure 4.10. These thermograms are quite similar to those of the composite magnesite. The main differences or trends which may be noticed in this series of thermograms are the following: the endotherm around 500°C due to huntite appears more distinctly in the finer fractions compared to its appearance as a shoulder to the major breunnerite endotherm on the low temperature side. This suggests that while huntite is present in all fractions there may be somewhat larger concentrations of the same in finer fractions. The second point to be noted is that the endotherm at 835°C is narrower and smaller in coarse fractions whereas the same endotherm appears broader and tends to split into two narrowly spaced distinct maxima. The tentative explanation offered for this is that while huntite is present in ^{more} ~~all~~ finer fractions giving rise to its characteristic endotherm at 835°C , ^{also} calcite and dolomite appear in a larger proportion in finer fractions causing a broadening and splitting of this endotherm. The third feature to be noted is that the endotherm characteristic of dehydroxylation of talc at about 1030°C becomes more prominent in the finer fractions and is essentially absent in size fractions coarser than 140 mesh.



IG. 4.6 D.T.A. PATTERN OF RAW ALMORA MAGNESITE'
(-8 + 20) # ON 15' GRINDING.

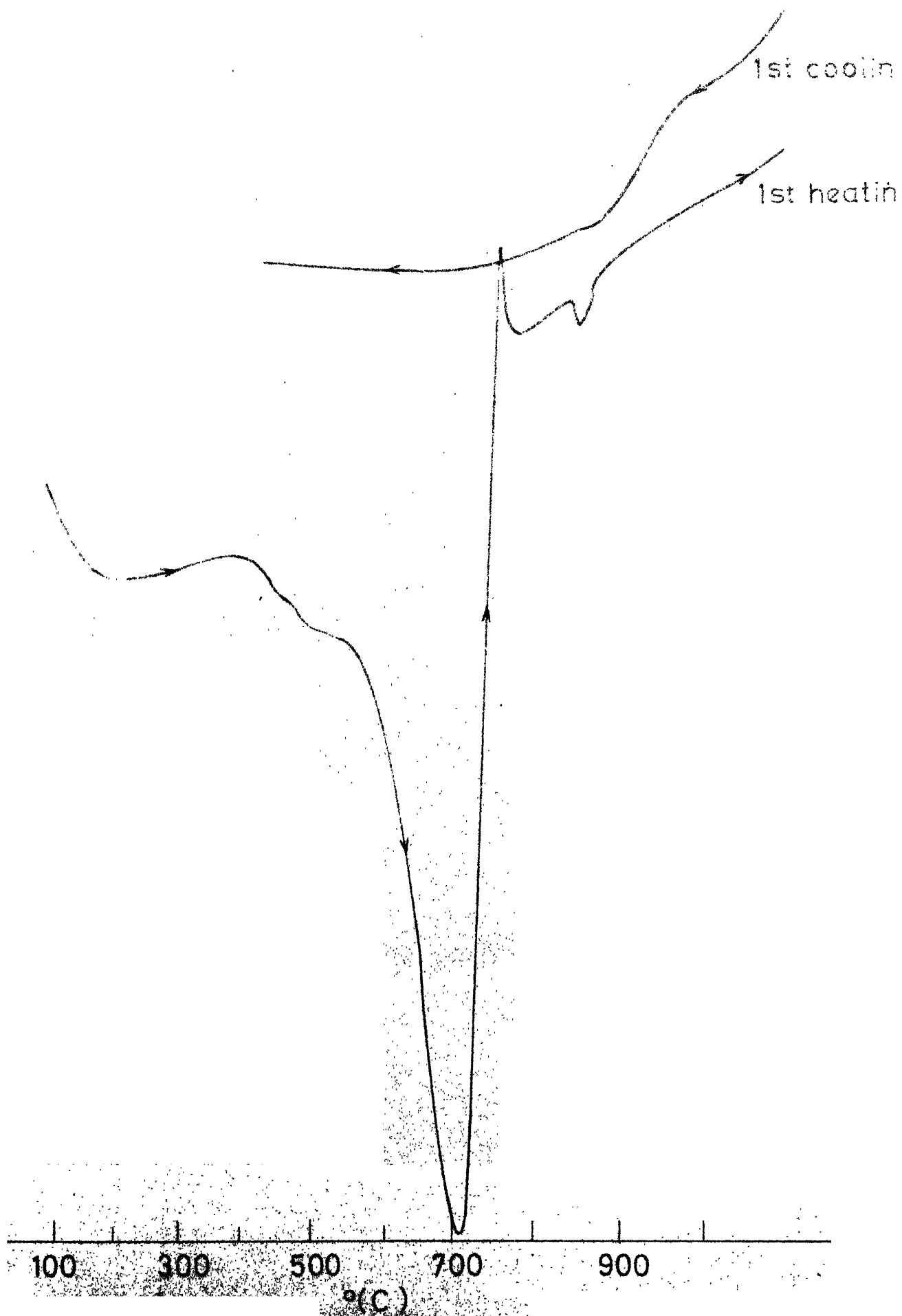


FIG. 4.7 DTA PATTERN OF RAW ALMORA MAGNESITE (-60+100

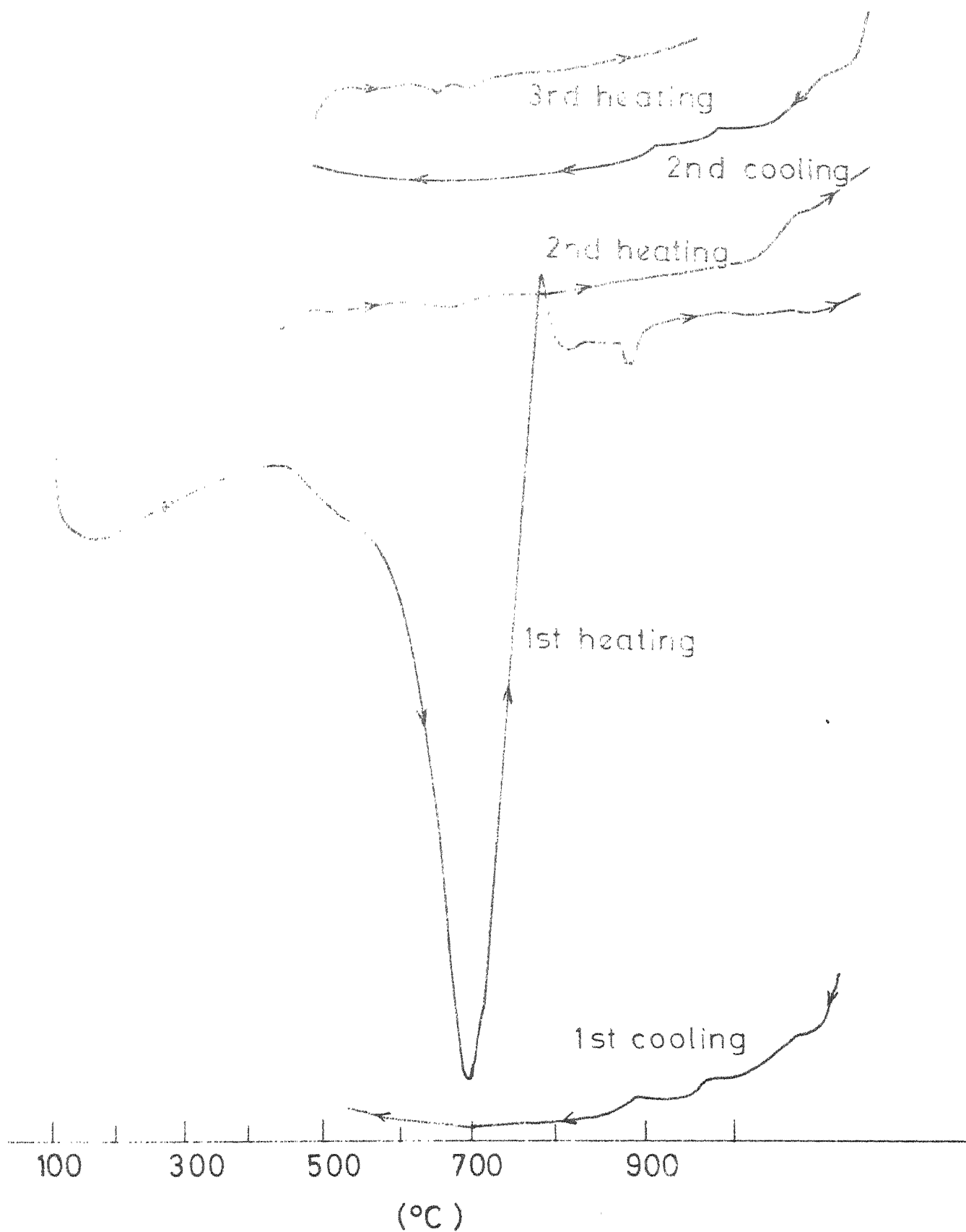


FIG.4-8 D.T.A. PATTERN OF RAW ALMORA MAGNESITE
(-140 + 230 #) 15' GRINDING.

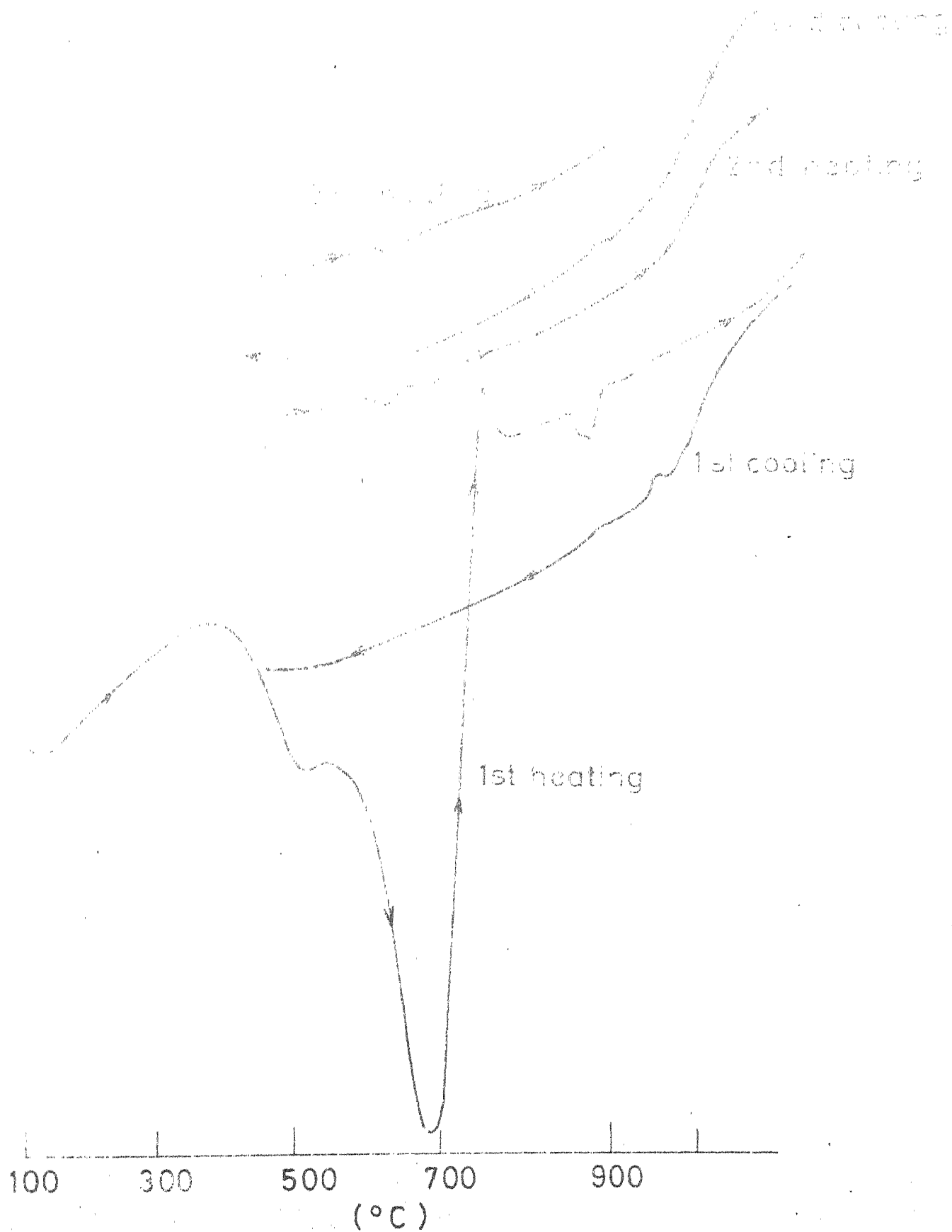


FIG. 4.9 D.T.A. PATTERN OF RAW ALMORA MAGNESITE
(-230 +270 #)

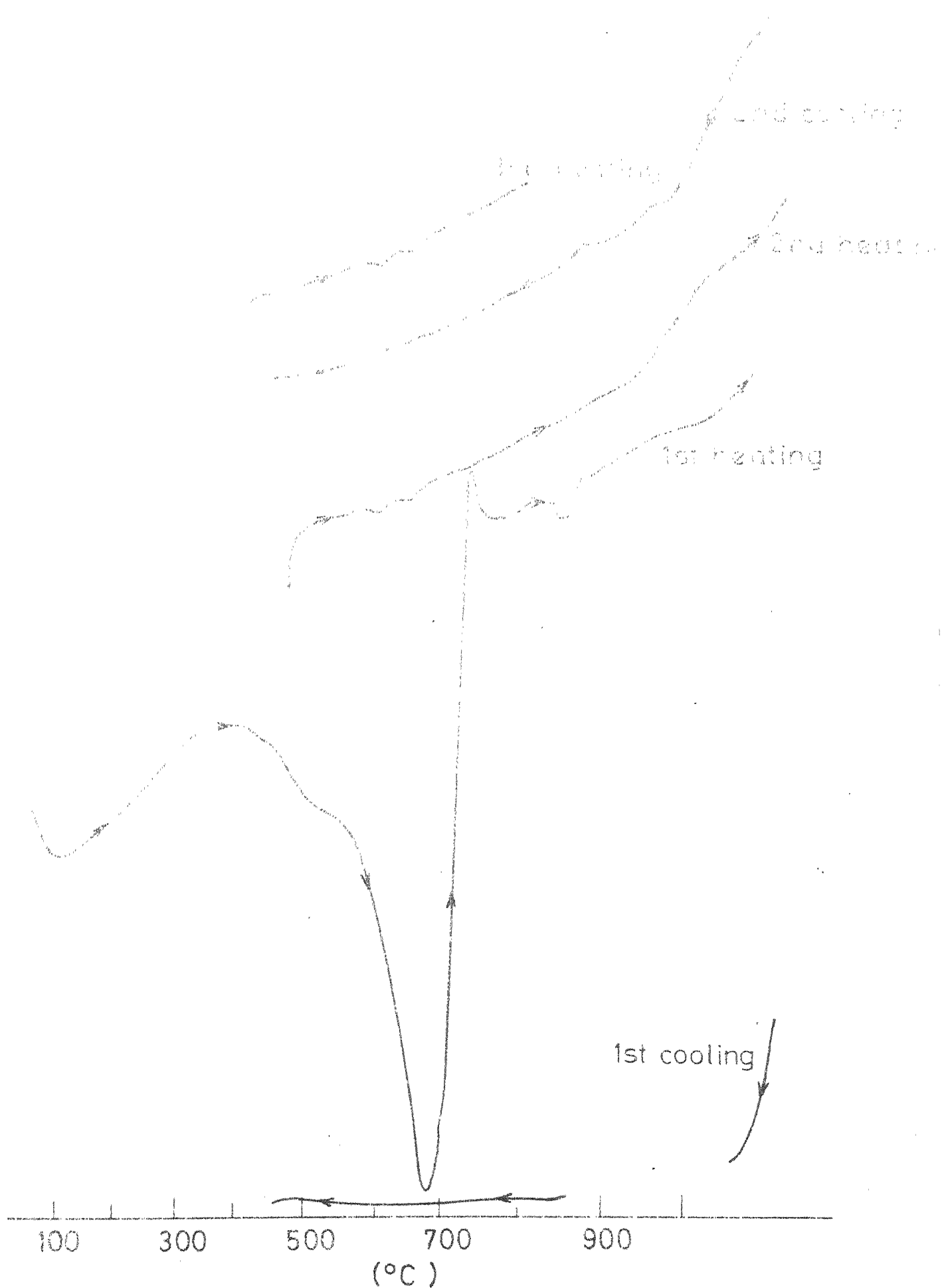


FIG. 4.10 D.T.A. PATTERN OF RAW ALMORA MAGNESITE
(-325 # ON 15' GRINDING)

The DTA data ^{are} is thus in broad general agreement with the X-ray diffraction results.

4.3 Heavy Liquid Separation of Calcined Almora Magnesite

The DTA results presented above show that breunnerite is decomposed to its constituent oxides by about 740°C, while the associated minerals namely huntite, dolomite, calcite and talc do not decompose at this temperature. Therefore Almora magnesite was calcined at 750°C for 2 hrs and 780°C for 3 hrs and 1200°C for 1 hr. These specimens were subjected to heavy liquid separation using bromoform, with specific gravity of 2.87. It was anticipated that periclase with a density of 3.5 would definitely sink and the other minerals which are present as impurities in smaller quantities would float on the top of the liquid. The X-ray diffraction pattern of the light fractions is shown in Figure 4.11. It may be noticed that the decomposition of magnesite is not completed until ~~at~~ 780°C, although only the most intense peak of magnesite persists in the samples calcined at 750°C and 780°C while the other reflections essentially disappear by this temperature. The discrepancy between this result and the DTA data may be due to the inaccuracy in the temperature measurement in the muffle furnace in which the samples were calcined. Magnesite is clearly absent in

the sample calcined at 1200°C. Dolomite and calcite continue to be present in an essentially undecomposed condition even after calcination at 780°C as indicated by their characteristic diffraction lines. However these carbonates also are decomposed by calcination at 1200°C. Talc becomes more prominent after calcination at 750°C and 780°C and disappears on calcination at 1200°C. At the same time forsterite appears in the sample calcined at 1200°C. It may be pointed out that the dehydroxylation of talc gives rise to forsterite. The fact that periclase lines are distinctly seen in the light fractions means that the heavy liquid separation has not been completely effective.

4.4 Sintered Magnesites of Almora, Salem and S. Korea

The sintered sample of the three magnesites were studied by X-ray diffraction and DTA.

The X-ray diffraction patterns over a selected range are shown in Figure 4.12. Periclase was found to be the predominant phase in all the three sintered samples. However, the Almora sample shows a large amount of undecomposed magnesite as well as undecomposed calcite whereas such undecomposed carbonates were not detected in the other two samples. This suggests that Almora magnesite has been sintered at a much lower temperature than the

other two samples. The presence of fairly large quantities of iron oxides in Almora magnesites (Table III.1) lead to the formation of magnesioferrite at the sintering temperature. On the other hand the large amount of silica present in Salen magnesites combines with magnesia to form substantial amounts of forsterite.

Differential thermograms of the three sintered samples are shown in Figure 4.13. All the three samples exhibit a broad hump at 140°C due to removal of adsorbed moisture.

All the three display endotherms at about 425°C which may be attributed to the decomposition of magnesium hydroxide. Apparently periclase in the sintered samples becomes hydrated on exposure to atmosphere. This tendency is the least in Salen sample. The sintered Almora sample shows endotherm at 295°C and 550°C due to the decomposition of calcium hydroxide. Thus the DTA study supports the X-ray results. The hydroxides are not detected in the X-ray patterns either because of their small quantity or due to their presence as a thin coating on periclase grains. However, the heat energy of dehydration of magnesium hydroxide is sufficiently large to get registered in DTA peak. This was verified by taking a synthetic mixture of



FIG.4.13 D.T.A PATTERNS OF ALMORA, SALEM AND S.KOREAN SINTERED SAMPLES

50% magnesium hydroxide with 95% Al_2O_3 by weight. While this amount of magnesium hydroxide could not be detected in X-ray study, the DTA data gave an unmistakable peak due to the decomposition of magnesium hydroxide.

4.5 Grinding Characteristics of Alnora and Salem Magnesites

It has been pointed out in an earlier section that some of the undesirable impurities appear to be concentrated in certain size fractions of ball milled magnesite. If certain size fraction are to be discarded to eliminate specific mineral species, it is necessary to know what proportions such size fractions represent in the total ground magnesite. For this purpose size distribution of Alnora and Salem magnesites before and after ball milling are shown in Table IV.4 and Figure 4.14 and Figure 4.15.

From the information given in the Table IV.4 it appears that Salem magnesite becomes finer than Alnora magnesite for same milling conditions. The same data are plotted on a log-log scale in Figure 4.16. From the coordinates of two chosen points from the plots of ground product of Alnora magnesite, the following equations can be written

$$1 = 1.7924 m + c$$

and

$$1.25 = 3.0792 m + c$$

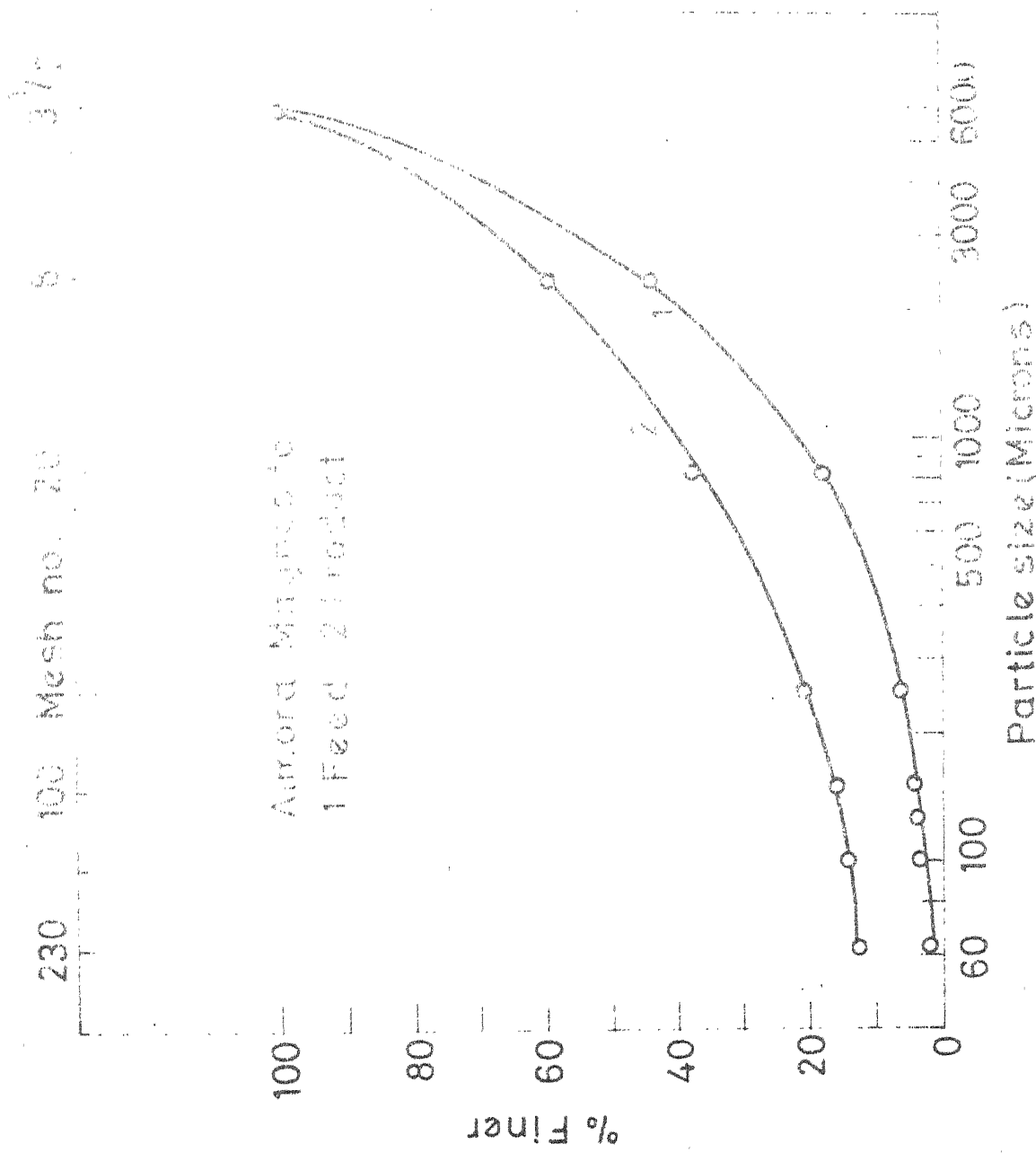


FIG.4.14 SEMILOG PLOT OF % FINER VS PARTICLE SIZE OF FEED AND PRODUCT OF GRINDING OF ALFORD MAGNESIA

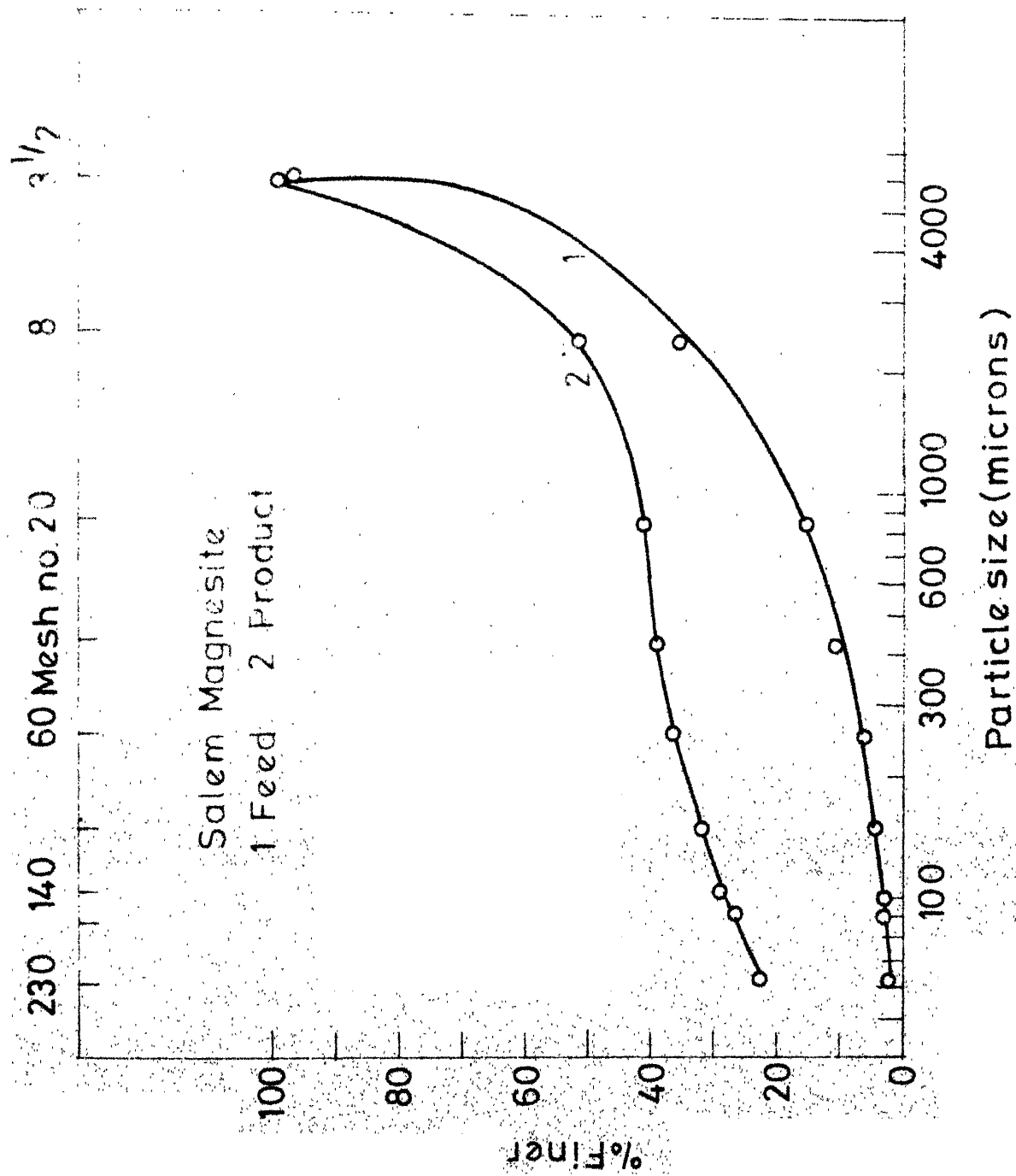


FIG.4.15 SEMILOG PLOT OF % FINER VS. PARTICLE SIZE OF FEED AND PRODUCT OF GRINDING OF SALEM MAGNESITE

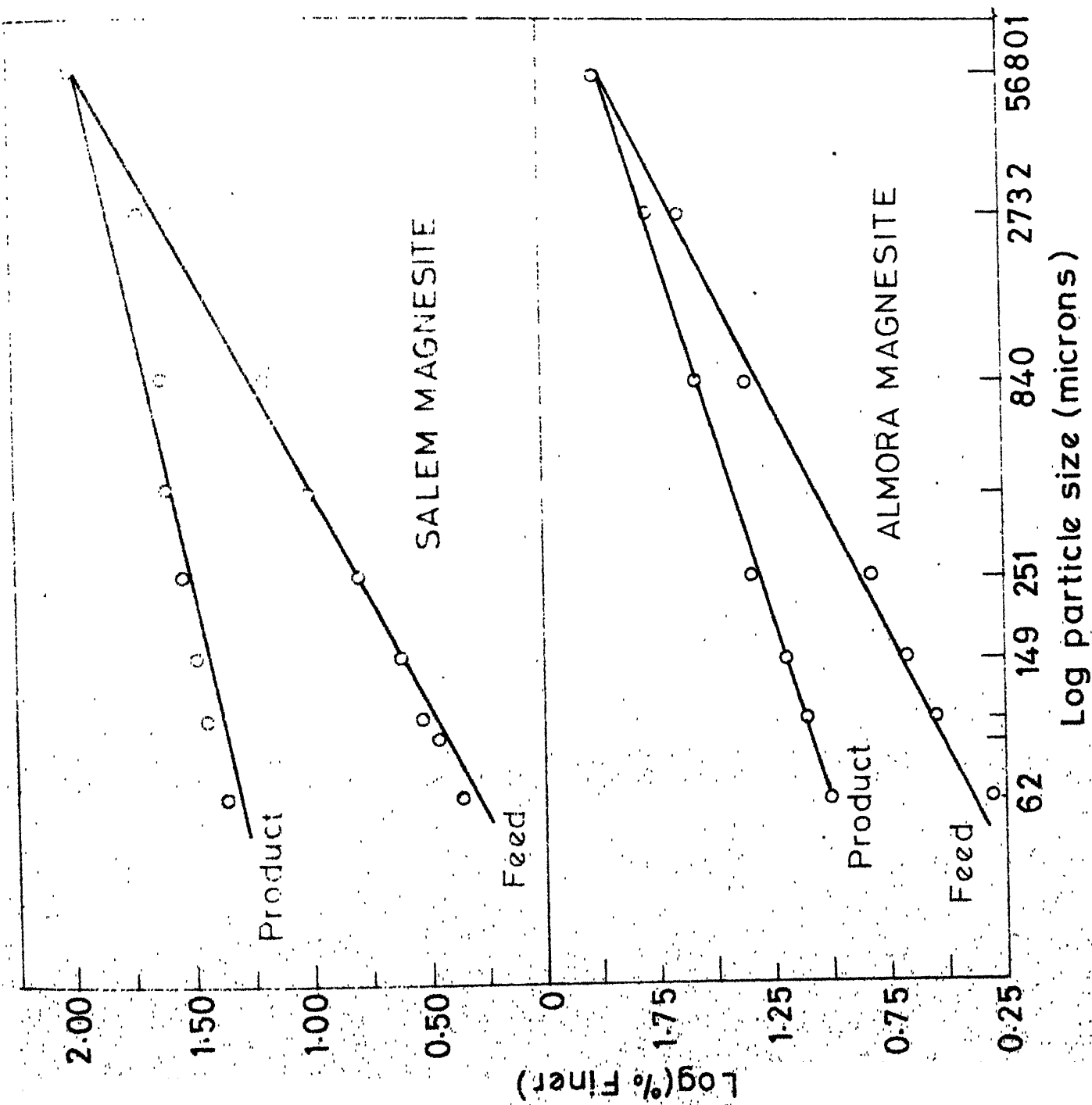


FIG. 4.16 LOG. LOG PLOT OF % FINER VS. PARTICLE SIZE OF FEED AND PRODUCT OF GRINDING OF MAGNESITES.

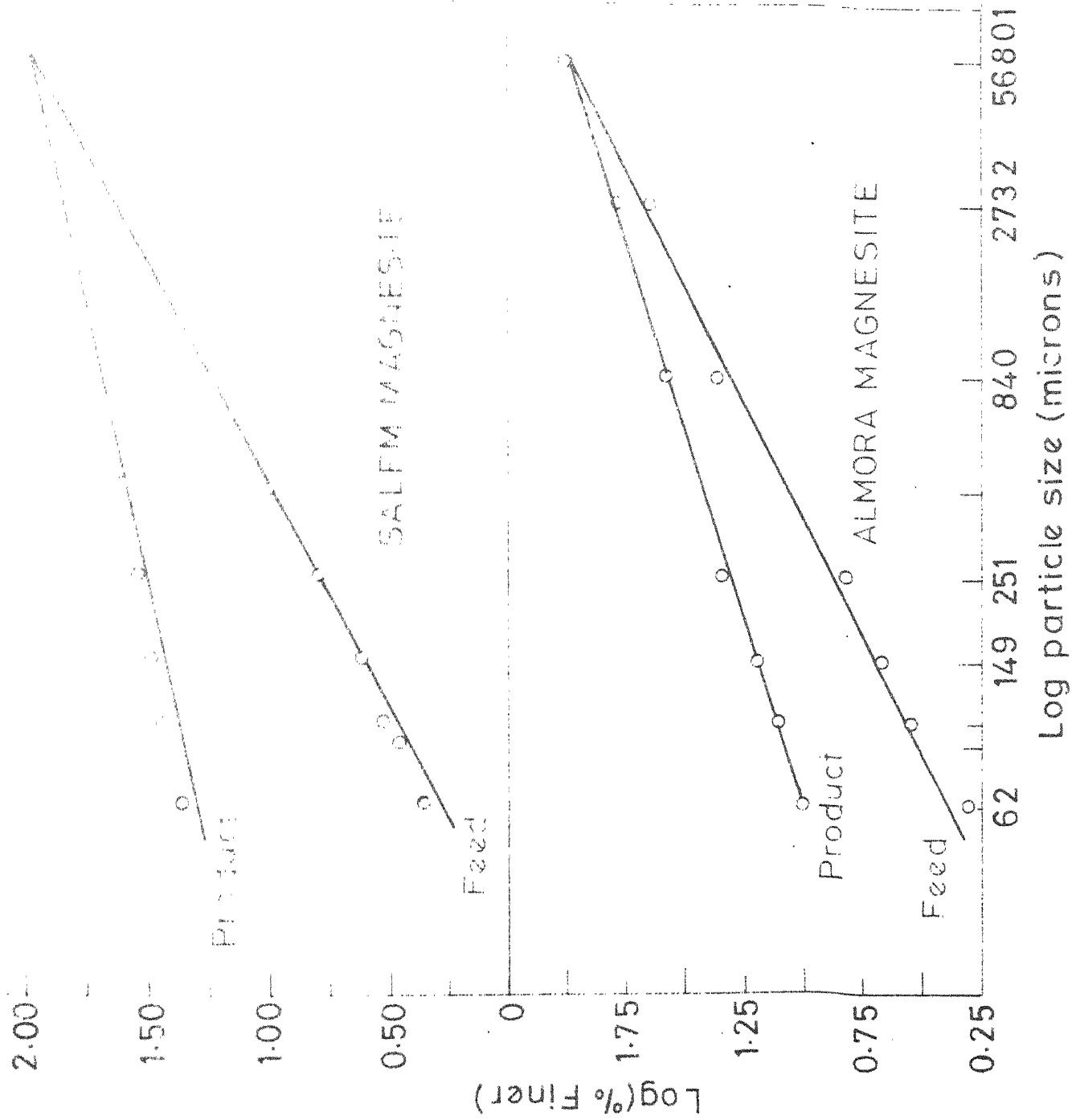


FIG. 4.16 LOG. LOG PLOT OF % FINER VS PARTICLE SIZE OF FEED AND PRODUCT OF GRINDING OF MAGNESITES.

Solving the above equations one gets,

$$m = 0.137 ,$$

$$c = 0.4219 .$$

$$\therefore \text{Log}(\% \text{ Finer}) = 0.137 \text{ Log}(\text{Size in microns}) + 0.4219$$

Similar procedure yields the following equation in the case of ground Salem magnesites

$$\text{Log}(\% \text{ Finer}) = 0.143 \text{ Log}(\text{Size in microns}) + 0.238$$

One may define a reduction ratio for a particular size as

$$\frac{\% \text{ product passing through}}{\% \text{ feed passing through}}$$

Values of reduction ratio for magnesite of 4 different sizes are listed in Table IV.4. These data also confirm that under identical conditions it is more difficult to grind Almora magnesite than Salem magnesite.

The data in Table IV.3 suggests that by eliminating material finer than 230 mesh removes most of the talc. Therefore rejection of about 10% of the ground material would reduce the silica content of magnesite significantly. If on the other hand even a larger proportion of silica should be removed, all material finer than 100 mesh has to be rejected. This constitutes about 16% of the material. Similarly in order to eliminate calcite

Table IV.2 Grinding Characteristics of Magnesites

Mesh size	Reduction ratio of Almora magnesite	Reduction ratio of Salem magnesite
8	1.345	1.460
20	2.086	2.650
60	3.163	5.816
140	3.477	8.416
230	5.023	9.601

Table IV.3 Variation in Calcite, Dolomite and Talc Abundance in Different Size Fractions

Size fraction (mesh)	Intensity of 100% calcite peak	Intensity of 100% dolomite peak	Intensity of 48% talc peak
	Intensity of 12% magnesite peak	Intensity of 12% magnesite peak	Intensity of 12% magnesite peak
	I (104)/I (022)	I (104)/I (022)	I (002)/I (022)
-8+20	5.73	0.909	0.116
-60+100	>5.73	1.307	0.116
-140+230	>6.18	1.450	0.273
-230+270	5.00	0.660	0.660

Table IV. Grinding Characteristics of Magnesites

Mesh size	Reduction ratio of Amora magnesite	Reduction ratio of Salem magnesite
8	1.345	1.460
20	2.086	2.650
60	3.163	5.816
140	3.477	8.416
230	5.023	9.601

Table IV.7 Variation in Calcite, Dolomite and Talc Abundance
in Different Size Fractions

Size fraction (mesh)	Intensity of 100% calcite peak	Intensity of 100% dolomite peak	Intensity of 48% talc peak
	Intensity of 12% magnesite peak	Intensity of 12% magnesite peak	Intensity of 12% magnesite peak
	I (104)/I (022)	I (104)/I (022)	I (002)/I (022)
-8+20	5.73	0.909	0.116
-60+100	>5.73	1.307	0.116
-140+230	>6.18	1.450	0.273
-230+270	5.00	0.660	0.660

and periclase material finer than 140 mesh should be discarded. This constitutes about 12.5% of the ground product. One of the suggestions therefore that emerges from this work is that Almora magnesite may be beneficiated with respect to lime and silica by grinding the materials for 15 minutes and discarding 10-15% of the fine material.

4.6 Effect of Calcium Carbonate on Almora Magnesite Sintered at 1700°C

Calcium carbonate up to 20 wt. % has been added to Almora magnesite and sintered at 1700°C followed by either fast or slow cooling. The resulting materials have been examined by X-rays. Periclase continues to be the predominant phase in all compositions. No noticeable line shift has taken place suggesting solid solution formation (Figure 4.17). There are no indications that any of the added lime is incorporated in the lattice. No silicate phase has also been observed. This is not surprising since silica content of Almora magnesite is quite small. The small amount of silica present combines with MgO to form forsterite in the sintered material. The added lime appears to remain as a second phase in all these compositions though it could be detected only in samples containing more than 4%.

In summary, therefore, it may be said that addition of calcium carbonate to Almora magnesite followed by sintering at 1700°C neither led to the incorporation of calcium in periclase lattice nor in the form of any silicate. Therefore this line of approach was not pursued further.

Almora magnesite, without any intentional addition of calcium carbonate, sintered at 1700°C was examined in Mossbauer spectrometer. The resulting spectrum is shown in Figure 4.4. Compared to the Mossbauer spectrum in the raw magnesite, in the calcined sample it does not show quadrupole splitting. This indicates that iron is present in a cubic environment. This would be the case whether iron is present as Fe^{2+} in cubic periclase phase or as Fe^{3+} in cubic magnesioferrite. A closer look at the shape of the absorption peaks indicates an asymmetric in the absorption peak which arises due to the simultaneous presence of iron in the 2^{+} and 3^{+} state. A rough comparison of the relative intensities of these two peaks suggests that most of the iron in the material sintered at 1700°C is present only in divalent state with limited amount in trivalent state. This implication of this is that sintered sample contains more magnesio-wustite than magnesioferrite. The X-ray evidence for magnesio-wustite which is a solid solution of FeO in MgO would simply consists of a small shift in the

diffraction lines. Such a shift indeed was observed as shown by the comparison of a few of the observed in specings with those of a standard periclase pattern.

<u>hkl</u>	<u>d_{obs}</u> ^o Å	<u>d_{std}</u> ^o Å
220	1.485	1.489
311	1.267	1.270
222	1.213	1.216

Another significant feature of the X-ray diffraction pattern is that each of the above lines is split into two at $d =$ 1.486 and 1.484, 1.268 and 1.265 and 1.215 and 1.212 respectively.

It is suggested that this doublet may indicate the coexistence of a fairly pure periclase with magnesiowustite. The lattice parameter turns out to be approximately 4.22 \AA . Compared to the fairly prominent lines of magnesiowustite, those of magnesioferrite are quite weak. This is in line with the Mossbauer results. The fact that the main absorption is due to divalent iron, and the shoulder appearing as an assymetric distortion of the peak, is supported by the isomer shift values.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions of this work are:

1. The presence of breunnerite in Almora magnesite is clearly established by X-ray, DTA, IR and Mossbauer studies.
2. Unequivocal evidence for the presence of huntite $Mg_3Ca(CO_3)_4$ in Almora magnesite is presented.
3. Dolomite, calcite and talc were the other minerals detected.
4. Grinding for a short duration followed by size fractioning could lead to a method for the elimination of undesirable impurities such as lime and silica. This may be accomplished by the rejection of ~~10 to 20%~~ of the finest fraction of the ground material, *amounting to 10 to 20% of the total*
5. Almora magnesite has been found to be somewhat more difficult to grind than Salem magnesite.

Further work along the following lines is suggested.

1. Promising results of the present study should be confirmed by treating larger quantities of the material along the lines of the present investigation.

2. The results of the present study should be made use of for beneficiation of Almora magnesite by gravity separation, particle size reduction and the other mineral engineering processes. The main aim of the study is to reduce the lime content ^{since} ~~and iron oxide~~ if it has a deleterious effect on the refractory properties.
3. Study of the refractories properties of different size fractions sintered to appropriate temperatures may establish a relationship between the mineralogical constitution and behaviour of the refractories.

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